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Aryl Insertion vs Aryl—Aryl Coupling in C,C-Chelated Organoborates: The "Missing Link" of Tetraarylborate Photochemistry

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Supporting Information

ABSTRACT: The photoreactivity of 9-borafluorene-based, C,Cchelated organoborates was investigated. Unlike the related tetraarylborates, the charge-transfer transitions imparted by the biphenyl chelate lead to selective insertion of one aryl substituent into the endocyclic B-C bond of the 9-borafluorene moiety, resulting in the formation of boratanorcaradienes. This photoreaction likely proceeds according to a Zimmerman rearrangement, which is analogous to one of the initially proposed mechanisms for tetraarylborates and provides additional insight into these long-debated photochemical reactions.

etraarylborates represent a class of anionic tetracoordinate l organoboron species with great significance in synthetic and analytical chemistry. Initially prepared by Wittig in 1947,¹ such molecules are frequently used as precipitating agents,² as weakly coordinating anions,³ and for base-free Suzuki-Miyaura-type cross-coupling reactions.⁴ In addition, tetraarylborates are known to undergo photoreactions upon exposure to strong UV light (254 nm), with the outcome of these experiments causing vigorous debate in the literature. Williams et al. were among the first⁵ to report on the irradiation of tetraphenylborates I (Scheme 1; R = H, M = Na) in water, wherein they isolated biphenyl, 1-phenyl-1,4-cyclohexadiene, and Ph₂BONa as major products.⁶ This distribution differed depending on whether irradiation was performed under N_2 (up to 97% 1-phenyl-1,4-cyclohexadiene) or air (ca. 59% biphenyl). Labeling studies revealed that the two benzene rings of the biphenyl product originated from the same Na[BPh₄] and that both of the carbon atoms linking the two rings were initially bound to the boron center. This photoreactivity was therefore rationalized as a variant of the di- π -methane rearrangement (i.e., Zimmerman rearrangement).⁷ Eisch et al. continued this investigation using tetraphenylborates in aprotic solvents (THF and DME). In their hands, irradiation under inert conditions afforded biphenyl and, upon the addition of diphenyl acetylene, a trapped borirene species II (Scheme 1). This finding led them to propose that photolysis of [BPh₄]⁻ generates the corresponding diphenyl-substituted anion [BPh₂]⁻ in solution.⁸ Schuster et al. reported a different interpretation of this photoreaction based on their isolation and structural determination of a borirane anion III by X-ray crystallography (Scheme 1).⁹ This deep red species was also characterized by NMR spectroscopy, with diagnostic chemical shifts at -26.6 (^{11}B) and 37.1 (^{13}C) ppm for the atoms of the three-membered



Scheme 1. Photoreactivity of Tetraarylborates



ring.⁹ The formation of III was once again explained according to the Zimmerman rearrangement, where excitation at 254 nm leads to an excited-state C-C-coupled biradical. The boron atom subsequently "walks" along the newly generated biphenyl to give the most stable borirane isomer.

Thus far, the photoreactivity of tetraarylborates has been heavily focused on compounds with four individual sub-

Received: May 15, 2018

stituents, with one important exception being the spiromolecule IV which is photochemically inert (Scheme 1).¹⁰

Considering these differing reactivities and the debate surrounding them, it is surprising that an intermediate case with one biphenyl C,C-chelating unit has not been studied.¹¹ We therefore set out to prepare anionic 9-borafluorene derivatives A with tetracoordinate boron atoms and various aryl substituents to examine whether they are also photoreactive and, if so, what types of products are generated via photolysis (e.g., [BAr₂]⁻ vs borirane). Irradiation of these new C,C-chelated compounds leads to structural rearrangement via selective arvl insertion into one of the endocyclic B-C bonds of $A_{r}^{11,12}$ forming boratanorcaradienes B which are related to the previously reported (aza)boratanorcaradienes (e.g., C, Scheme 1) generated from neutral C,N- or C,(NHC)-chelate systems (NHC = N-heterocyclic carbene).^{13,14} Unlike the work of Williams, Eisch, and Schuster for I, no aryl-aryl C-C coupling product (D) was observed upon irradiation of A, regardless of the aryl substituents utilized. Mechanistically, the photochemical reaction of A likely follows a Zimmerman rearrangement, where charge-transfer transitions introduced by the biaryl chelating unit govern the selectivity of the reaction.¹⁵ The details are presented herein.

There exist few examples of tetracoordinate 9-borafluorene anions in the literature, with each requiring elaborate synthetic strategies.¹⁶ We developed a new two-step protocol starting from 2,2'-dilithiobiphenyl (for Li[1^H]-Li[3^H]) or its 4,4'-tert-butyl-substituted derivative (for Li[1^{fBu}]-Li[3^{fBu}]) and the appropriate borane, followed by cation exchange with KO'Bu. Compounds K[1^{H/fBu}]-K[3^{H/fBu}] were thereby prepared in moderate to good yields (see Scheme 2 and Supporting

Scheme 2. Synthesis of 5*H*-Dibenzo[*b*,*d*]borol-5-ides $M[1^{H/tBu}]-[3^{H/tBu}]^{a}$



^aCarbon atoms marked with asterisks bear H or tBu substituents.

Information (SI) for details). All of the compounds were fully characterized by ¹H, ¹¹B{¹H}, and ¹³C{¹H} NMR spectroscopy as well as HRMS. The crystal structures of Li[1^H], Li[1^{IBu}], Li[2^H], and Li[3^{fBu}] were determined by single-crystal X-ray diffraction (see SI). The B–C bond lengths in Li[1^H], Li[1^{fBu}], Li[2^H], and Li[3^{fBu}] (1.628(8)–1.678(4) Å) are comparable to those of other C,C-chelate 5*H*-dibenzo[*b*,*d*]borol-5-ides as well as the neutral B,N-analogues.^{14b,16,17}

Compounds $\mathbf{K}[\mathbf{1}^{H/tBu}] - \mathbf{K}[\mathbf{3}^{H/tBu}]$ all absorb intensely ($\varepsilon = 6900-26400 \text{ M}^{-1}\text{cm}^{-1}$) in the UV region between 300–340 nm as shown in Figure 1. These values are bathochromically shifted relative to those of tetraarylborates ($\lambda_{\text{max}} \approx 275 \text{ nm}$)^{9b,13b} and blue-shifted compared to the π -extended C, (NHC)-chelates of Yamaguchi and co-workers.^{13a} TD-DFT calculations of $[\mathbf{1}^{H/tBu}]^{-}-[\mathbf{3}^{H/tBu}]^{-}$ and $[\text{BPh}_4]^{-}$ reveal that the computed S₁ and S₂ transitions are close in energy and correspond to HOMO \rightarrow LUMO and HOMO-1 \rightarrow LUMO respectively (see Figure 1 and the SI). For $[\text{BPh}_4]^{-}$, both HOMO and HOMO-1 are of π -Ph character and mainly



Figure 1. (Left) UV–vis spectra of $K[1^{H/tBu}]-K[3^{H/tBu}]$ and $K[1^N]$ (cf. Figure 4) in CH₃CN at 10^{-4} M. (Right) Orbital diagrams of the calculated S₁ and S₂ transitions for $K[1^H]$.

localized on two of the four phenyl rings, while the LUMO is delocalized across all four phenyl substituents (π^* -Ph). Although compounds $[1^{H/tBu}]^--[3^{H/tBu}]^-$ share a similar HOMO \rightarrow LUMO (π -biPh $\rightarrow \pi^*$ -biPh) transition, the HOMO-1 resides on the aryl substituents (π -Mes/p-Tol). As a result, the corresponding absorption bands of $[1^{H/tBu}]^--[3^{H/tBu}]^-$ can be assigned as having mixed $\pi \rightarrow \pi^*$ and charge-transfer (CT) character. This is related to the neutral N,C-chelate systems, which show dominant CT character for their S₁.^{14a} Bidentate chelation of boron therefore introduces accessible CT transitions, which are known to contribute to the unique photoreactivity of these types of systems.¹⁸

Irradiation of $Li[1^H]$ or $Li[1^{tBu}]$ with UV light (300 nm) in dried/degassed CD₃CN causes the initially colorless solutions to become dark orange or red. Monitoring this transformation by NMR spectroscopy reveals the conversion of $Li[1^{H}]$ to a new species with one ¹¹B resonance at -22.4 ppm (see the SI), comparable to that of III (-26.6 ppm). Unlike the borirane anion of Schuster et al. which displays cyclohexadienyl and Hborirane ¹H NMR signals at 5.55 and 1.39 ppm, respectively, our photoproduct is characterized by two cyclohexadiene singlets at 5.41 and 4.81 ppm (1:1) and six signals of equal intensity for the chemically inequivalent methyl groups. The most upfield-shifted signal (0.16 ppm) belongs to the methyl group located on the $C(sp^3)$ atom. Although this species is expected to be of type B (Scheme 1), its tendency to decompose, even at room temperature (see SI), prevented full spectroscopic characterization. To circumvent this issue, the Li⁺ counterion was exchanged for K⁺. Repeating the photolysis experiment with $K[1^H]$ gives the same NMR-spectroscopic data (Figure 2 and SI), where the borirane photoproduct $K[1^{H}a]$ is now stable indefinitely at room temperature under an inert atmosphere. 2D NMR analysis confirms the identity of the photoproduct to be the boratanorcaradiene derivative $K[1^{H}a]$, which is related to known (aza)boratanorcaradienes (e.g., C, Scheme 1)^{13,14a} and therefore most likely generated via a di- π methane rearrangement.¹⁵ Similar to the phototransformations of C₁(NHC)-chelated organoborates,¹³ this aryl insertion is not thermally reversible even up to $120 \,^{\circ}\text{C}^{.19}$ It is worth noting that K[1^H] undergoes exclusive aryl insertion into a B-C bond of the 9-borafluorene backbone, with no aryl-aryl coupling as demonstrated for I. This is believed to be a result of the S₁ and S_2 transitions, whose $\pi \rightarrow \pi^*$ and CT character do not facilitate aryl–aryl coupling. The analogous transformation was also observed for $K[1^{fBu}] \to K[1^{fBu}a]$ (see SI). To investigate the possibility of trapping a borene anion from the photoreaction of

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Figure 2. (Left top) ¹H NMR spectra (400.13 MHz, CD_3CN) showing the conversion of colorless $K[1^H]$ (spectrum a) to red $K[1^Ha]$ (spectrum c) via the stage of a clean mixture (spectrum b) upon irradiation ($\lambda = 300$ nm) in a sealed NMR tube over 5 h. (Left bottom) UV–vis tracking of the conversion of $K[1^H]$ (black curve) to $K[1^Ha]$ (red curve) upon irradiation ($\lambda = 300$ nm). (Right) crystal structure of $K[1^Ha]$ (H atoms are omitted for clarity).

 $K[1^{\rm H}]$, 1,2-bis(4-*tert*-butylphenyl)ethyne was added to solutions of $K[1^{\rm H}]$ before photolysis and $K[1^{\rm H}a]$ once it was formed. Both attempts failed to yield the desired borirene, even when $K[1^{\rm H}a]$ and alkyne were heated to 80 °C, suggesting that the borirane $K[1^{\rm H}a]$ is more stable than the photoproduct of tetraphenylborates as described by Eisch.

Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a saturated CH₃CN solution containing K[1^Ha]. The internal bond angles of the central three-membered ring are close to ideal (B–C–C: 59.6(2)° and $61.9(2)^{\circ}$; C–B–C: 58.5(2)°), which is in line with previous reports on borirane structures.²⁰ The K⁺ ion is positioned between one Mes and one C₆H₄ ring of the backbone from a neighboring molecule with the distance between the K⁺ ion and the centers of the aryl rings being 2.884(3) and 3.000(3) Å, forming an extended 1D-structure. Furthermore, the K⁺ ion has short contacts of 3.367(3) and 3.607(3) Å with a C=C bond of the cyclohexadienyl fragment. One acetonitrile molecule is coordinated to the cation with a K–N distance of 2.818(3) Å.

Tracking the photoreaction of K[1^H] by UV-vis spectroscopy reveals a decrease in its main absorption band at λ_{max} = 324 nm with the concomitant appearance of a new, broad absorption band belonging to $K[1^{\hat{H}}a]$ that ranges from 320-600 nm. Continued irradiation eventually results in full conversion to the photoproduct, with $\lambda_{\max} \approx 436$ nm and $\varepsilon =$ 3400 M^{-1} cm⁻¹ (for a corresponding study on K[1^{tBu}], see the SI). TD-DFT data suggest that this low-energy band originates from CT from HOMO (π -trimethylcyclohexadiene and borirane) to LUMO (π^* -biPh), which is in agreement with (aza)boratanorcaradienes.¹⁸ The absorption profile of $K[1^{H}a]$ shares some similarities with C,(NHC)-stabilized boriranes $(\lambda_{\rm max} \approx 430 \text{ nm})$,¹³ which absorb at a much higher energy compared to the N,C-variants ($\lambda_{max} \approx 600$ nm). This is attributed to LUMO destabilization by C,C/C,(NHC)-chelation (see the SI).^{13b} The photoisomerization quantum efficiencies (Φ_{PI}) of $K[1^H]$ and $K[1^{fBu}]$ were determined to be 0.83 and 0.79 respectively, which is comparable to that of the N,C-chelate analogues.¹⁸



Figure 3. Photoreactivity of $K[2^{H/tBu}]$ (top) and $K[3^{H/tBu}]$ (bottom) upon irradiation at $\lambda = 300$ nm in CH₃CN under an inert atmosphere; carbon atoms marked with asterisks bear H or *t*Bu substituents.

To further explore the selectivity of these photoreactions, unsymmetric borates $K[2^H]$ and $K[2^{tBu}]$ were examined for their response to UV irradiation (Figure 3, top). Similar to $K[1^{H}]$, photolysis of $K[2^{H}]$ in CD₃CN with 300 nm light results in the formation of $K[2^{H}a]$, which was identified by its distinct ¹H and ¹¹B NMR resonances at -0.25 (d, ³J_{H-H} = 5.9 Hz; borirane-H) and -25.1 ppm, respectively. The absence of any singlets in the upfield region of the ¹H NMR spectrum indicates that the reaction is completely selective for the *p*-tolyl substituent, similar to the related N,C-systems.^{14b} Again, no aryl-aryl C-C coupling was observed. $K[2^{H}a]$ possesses a similar absorption profile as $K[1^{H}a]$, with a new broad band centered at $\lambda_{max} = 409$ nm ($\varepsilon = 2400$ M⁻¹cm⁻¹). The photoreactivities of $K[2^H]$ and $K[2^{fBu}]$ were found to be the most efficient of the series, with $\Phi_{\rm PI}$ near unity (0.98 for K[2^H] and 0.92 for $K[2^{tBu}]$). This finding is quite different compared to the N,C-analogues, which display a reduction in Φ_{PI} with similar substituents.^{14b} The subsequent H-migration observed in the unsymmetric N,C-chelate system^{14b} was not detected in $K[2^{H}]$ and $K[2^{tBu}]$, which may account for their high photoisomerization quantum efficiency.

It is known that diphenyl substituted N,C-chelate boron compounds are photochemically inert,¹⁷ which is in stark contrast to I. Considering that our biphenyl-chelated borates possess similarities between both of these systems, we decided to investigate also the photoreactivity of $K[3^H]$ and $K[3^{tBu}]$, which feature two p-tolyl substituents at boron (Figure 3, bottom). Following short irradiation times (15 min) at 300 nm, the ¹H and ¹¹B NMR spectra of K[3^H] and K[3^{tBu}] show a significant decrease in signal intensity of the starting material and a large number of overlapping emergent peaks. These C,Cchelate borates are therefore unstable toward irradiation and clearly operate according to a different photochemical pathway compared to tetraarylborates. This finding also supports the importance of the CT transition in the formation of boratanor caradienes, as the CT character of $K[3^{\rm H}]$ and $K[3^{\rm tBu}]$ is much less compared to $K[1^H]$ and $K[1^{fBu}]$ (see the SI for TD-DFT oscillator strengths).

Given that the C,C-chelate borates seem to follow analogous photoreactivity of the N,C-chelate compounds, the role of the N-atom was probed by preparing K[1^N] (Figure 4), which was also found to be photoresponsive at 300 nm in CH₃CN, changing from colorless to orange. The UV–vis spectrum shows a new broad band in the region between $\lambda = 350-550$ nm with a shoulder at $\lambda = 505$ nm. The ¹¹B NMR spectra



Figure 4. Photoreactivity of $K[1^N]$ upon irradiation at $\lambda = 300$ nm in CH₃CN under an inert atmosphere.

revealed two new resonances at -22.3 and -22.6 ppm, respectively, which correspond to the two potential photoisomerization products ($K[1^Na]$ and $K[1^Na]$ -*iso*) that can be formed upon irradiation of $K[1^N]$. Monitoring the reaction with ¹H NMR spectroscopy reveals a 2:1 ratio of the two isomers (see the SI for NMR analysis), whereby insertion into the B–C_{py} bond ($K[1^Na]$) is favored, possibly due to greater stabilization of the excited-state biradical when localized on py and mesityl vs phenyl and mesityl.¹⁵ The photoisomerization reaction of $K[1^N]$ proceeds with a comparable efficiency ($\Phi_{PI} =$ 0.76) to other C,C-chelate species.

In conclusion, we have prepared a series of organoborates with a biphenyl chelating unit and two varying aryl substituents. Examination of their photoreactivity reveals that they do not behave in accordance with tetraarylborates, likely due to their differing electronic transitions imparted by chelation. Instead, selective insertion of one aryl substituent into an endocyclic B-C bond yields boratanorcaradienes with an embedded borirane ring. These findings are in line with previous reports on N,C-chelate organoboron systems, suggesting that a similar CT-induced Zimmerman rearrangement is responsible for this unique transformation. Although the photoreactions are not thermally reversible, the efficiency of the photoisomerizations was found to be exceptionally high. Mechanistically, it would appear as though the C,C-chelated organoborates behave in line with the initial postulations of Williams and Schuster, thereby filling in the missing photoreactivities of this class of molecules.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.8b01534.

Experimental details and NMR data of $\text{Li}[1^{H/fBu}]$ – $\text{Li}[3^{H/fBu}]$, $\text{Li}[1^N]$, $\text{K}[1^{H/fBu}]$ – $\text{K}[3^{H/fBu}]$, $\text{K}[1^N]$, K- $[1^{H/fBu}a]$, $\text{Li}[1^N]$, $\text{K}[1^Na]$, and $\text{K}[1^Na]$ -iso; NMR monitoring of the photoisomerization of $\text{K}[1^{H/fBu}]$ – $\text{K}[3^{H/fBu}]$ and $\text{K}[1^N]$; photophysical properties of $\text{K}[1^{H/fBu}]$ – $\text{K}[3^{H/fBu}]$ and $\text{K}[1^N]$; UV–vis photoisomerization data of $\text{K}[1^{H/fBu}]$, $\text{K}[2^{H/fBu}]$, and $\text{K}[1^N]$; kinetic data for Φ_{PI} of $\text{K}[1^{H/fBu}]$, $\text{K}[2^{H/fBu}]$, and $\text{K}[1^N]$; x-ray crystal structure analyses of $\text{Li}[1^H]$ ·(thf)₄, $\text{Li}[1^{fBu}]$ · (thf)₄, $\text{Li}[2^H]$ ·(thf)₄, $\text{Li}[3^{fBu}]$ ·LiCl·(thf)₅, $\text{H}[1^N]$ ·Et₂O, $\text{K}[1^Ha]$ ·CH₃CN, Tol₂BCl, and 2,6-dimethyl-pyrimidin-4amine; computational details for compounds $\text{K}[1^{H/fBu}]$ – $\text{K}[3^{H/fBu}]$, $\text{K}[1^N]$, $\text{K}[1^{H/fBu}a]$, $\text{K}[2^{H/fBu}a]$, $\text{K}[1^Na]$, K- $[1^Na]$ -iso, and $[BPh_4]^-$ (PDF) Cartesian coordinates (XYZ)

Accession Codes

CCDC 1843173–1843180 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

J.R. did the experimental work; S.K.M. performed calculations; J.R. and S.K.M. contributed equally to the process of writing; M.B. conducted the X-ray diffraction, and the structure determination of Tol₂BCl, 2,6-dimethyl-pyrimidin-4-amine, $Li[1^{H}]\cdot(thf)_{4}$, $Li[1^{HBu}]\cdot(thf)_{4}$, $Li[2^{H}]\cdot(thf)_{4}$, $Li[3^{HBu}]\cdotLiCl\cdot$ $(thf)_{5}$, and $H[1^{N}]\cdotEt_{2}O$; $K[1^{H}a]\cdotCH_{3}CN$ was contributed by S.W.; H.-W.L. and M.W. supervised the experiments; S.W. and M.W. supervised the writing process.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

J.R. thanks the "Vereinigung von Freunden und Förderern der Johann Wolfgang Goethe-Universität" for a travel grant. S.K.M. thanks the Canadian Government for the Vanier CGS-D. Dr. Alexander Hübner (Goethe-Universität Frankfurt) contributed to this publication by crystallizing compound $\text{Li}[1^{H}] \cdot (\text{thf})_{4}$.

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